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(54) [Title of the Invention]

BINDERS FOR GLASS FIBER AND GLASS FIBER CLOTH

(57) [Abstract]

[Problem] To provide glass fiber cloth with good resin impregnation properties.

[Means of Solving the Problem] Inorganic solid particles such as 5—2,000 nm colloidal silica or soft calcium carbonate were admixed with the binder to be applied when spinning glass fiber. Applying this binder makes the par-

ticles adhere around the glass fiber used to form the yarn and creates spaces, hence cloth woven from this yarn can be well impregnated with a resin.

[Scope of the Patent Claim(s)]

[Claim 1] Binder for glass fiber to be heat deoiled, characterized in that it contains inorganic solid particles.

[Claim 2] Binder for glass fiber as described in Claim 1, characterized in that at least one type of inorganic solid particles selected from among colloidal silica, soft calcium carbonate, kaolin, and fine particulate talc with average particle sizes of 5—2,000 nm is contained in the binder applied to the glass fiber.

[Claim 3] Glass fiber cloth consisting of glass fiber yarn to which 0.001—2.0 weight% as solids of inorganic solid particles as described in Claim 2 has been applied.

[Detailed Description of the Invention]

[0001]

[Field of Industrial Application] The present invention pertains to a glass fiber binder and glass fiber to which this binder has been applied.

[0002]

[Conventional Techniques] A binder for glass fiber is applied to a large number of glass filaments immediately after spinning by a roller applicator or a belt applicator in order to protect the glass fiber, when preparing the glass fiber by spinning molten glass at high speed. Binders for glass fiber can be roughly classified into those for yarn and those for roving. Binders for yarn will be explained in the following. A glass fiber bundle coated with a binder is wound onto a cylinder in the form of a cake. The cake is dried to a certain degree and twine is produced by a twiner and wound onto a bobbin to

ticles adhere around the glass fiber used to form the yarn and creates spaces, hence cloth woven from this yarn can be well impregnated with a resin.

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thus obtain glass fiber yarn. The yarn is woven mainly into cloth, which is then subjected to a deoiling treatment such as thermal deoiling which removes the binder by thermally oxidizing it at high temperatures, or to water deoiling which removes the binder by water washing or in a vibrowasher, and then a surface treatment agent such as a silane coupling agent which improves bondability with a resin and heat resistance, is generally applied to the glass fiber surface.

[0003] This cloth is then impregnated with an uncured resin or with a resin which contains a solvent and is thus reduced in viscosity, and evaporated with the solvent, and then these cloths are stacked and pressed and thereby made into a laminate. The binders that are conventionally used for this purpose are those made mainly of starch, which prevent fiber fuzz and moreover can easily be removed

[0004] Recently, however, some binders for yarn have used materials based on synthetic resins such as PVA (polyvinyl alcohol), urethane resins, or epoxy resins. Starches for starch paste include various processed products, and can be found in the following forms: natural unprocessed starches, for example, starches such as cornstarch and potato starch, and chemically modified products of these, for example, etherified products such as hydroxyalkylated products, esterified products such as acetylated products, crosslinked products produced by reaction with a crosslinking agent such as epichlorohydrin, and low-viscosity products with the viscosity reduced by decreasing the well-known starch molecular weight by acid treatment, etc. Specifically, one example of a formulation of conventional binders using these starches consist of 2–10 weight% starch-based material, 0.2–5 weight% lubricant, 0.05–1.0 weight% surfactant, 0.01–0.5 weight% preservative, with the remainder con-

sisting of water.

[0005] Starch is used for the purpose of bonding and assembling several hundred filaments into one strand and forming a film in order to protect the yarn from all mechanical flexing and friction. Corn and potato are used often as raw materials for starch, and their chemically modified products, for example, etherified products such as hydroalkylated products, are used often. A lubricant is used for the purpose of providing the strand with slipping properties, thus reducing mechanical friction and protecting the yarn. The types of lubricants used often include hydrogenated oils produced by adding hydrogen to animal and vegetable oils, paraffin wax, and esters of higher saturated fatty acids with higher saturated alcohols. Cationic lubricants are used for the purpose of softening the glass yarn and reducing friction between filaments in the strand; for example, alkyl quaternary ammonium salts, and amides or imidazolines that can be obtained by a condensation reaction of a polyethylene polyamine with a higher fatty acid, are often used. A surfactant is used mainly as an emulsifier for the lubricant; for example, polyoxyethylene alkyl ethers are often used. Formalin is mainly used as a preservative.

[0006] Japanese Kokoku No. 1[1989]-203,247 discloses a glass fiber roving binder for the spray-up of a FRP, which is produced by mixing colloidal silica in polyvinyl acetate, as a glass fiber treatment agent in which the colloidal silica is admixed in the form of solid particles. Furthermore, Japanese Kokai No. 6[1994]-248,572 discloses a technique in which glass fiber cloth is impregnated with colloidal silica and then dried. The tow of the glass fiber cloth is then opened by a vibrowasher, the cloth is impregnated with a resin, and pieces of the cloth are stacked and hot pressed. The former technique is used to improve the cutting properties by the application of a

binder that contains colloidal silica and thereby makes it more difficult for the glass fiber roving to slip. The latter technique is applied to make the resin permeate more easily by impregnation of the glass cloth with colloidal silica, and then the tow is opened by means such as a vibrowasher, thereby letting the colloidal silica pass between the glass fibers and create spaces between the fibers. However, because the warp and weft cross each other in the cloth, it has been very difficult to make the colloidal silica pass uniformly into the various detailed parts.

[0007]

[Problem to be Solved by the Invention] Binders that are formed of a combination of these compounds have considerable good characteristics, and in fact have actually been used. However, as the speed and efficiency of producing glass fiber are increased, and as the amount of glass fiber wound at a time is increased gradually, in order to increase the size of the cake, i.e., to make a larger cake package, some fibers in the cake get severed and the amount of fuzz on the glass fiber yarn increases. This phenomenon presumably occurs for the following reasons: As the amount of glass fiber wound onto a cylinder increases, the diameter increases and the tension applied to the glass fiber gradually increases as the winding progresses. Eventually the force that is generated is great enough to crush the inner layers of glass fiber, which in turn severs some of the glass fibers. On the other hand, it is hoped that the problem can be solved. Presumably the manufacturing cost of the laminates can be reduced by shortening the time of impregnating with a resin the glass fiber cloth woven of glass fibers and by increasing the efficiency of manufacturing the laminates.

[0008] The present invention pertains to a binder for glass fiber that

has been newly developed to solve the problems mentioned above. The goal of the present invention is to provide a binder which has an excellent ability to stabilize the shape of the cake during glass fiber spinning, and which can help to provide glass fiber yarn with extremely little fuzz even as seen in a processing step with the conventional amount of winding, and even when the amount of winding is increased. Furthermore, the invention binder provides the woven glass fiber cloth with good resin impregnation properties and provides glass fiber to which this binder has been applied.

[0009]

[An Approach to Solving the Problems] The present invention solves the above-mentioned problems by admixing at least one type of inorganic solid particles such as colloidal silica, kaolin, or soft calcium carbonate into a binder for glass fiber, and applying 0.001–2.0 weight% as solids of these solid particles to the glass fiber.

[0010]

[Embodiments of the Invention] The goal of the present invention is to solve the aforementioned problem by adding inorganic solid particles such as colloidal silica to such a binder, however some surfactants are not compatible with colloidal silica and when such surfactants are added gelling or separation could occur. Accordingly, the binder components to be combined are selected by taking this fact into consideration. Inorganic solid particles are not only effective for a conventional type of binder when the main binder component consists of starch. They are also effective when materials based on synthetic resins such as PVA (polyvinyl alcohol), urethane resin, and epoxy resin are used. Inorganic solid particles that can be used in the present invention include kaolin, soft calcium carbonate, fine particulate talc, pow-

dered fumed silica (produced by Nippon Aerojil Co.), and colloidal silica. These particles should not decompose at the heat deoiling temperatures, and the particles sizes that can be used range from 5 to 2,000 nm.

[0011] The colloidal silica is such that amorphous silica with particle sizes of about 5–100 nm can be dispersed stably in water or in an organic solvent without settling, and is also called silica sol. This colloidal silica can be obtained by highly polymerizing silicic acid that can be obtained by hydrolyzing an aqueous solution of sodium silicate (water glass), silicic acid esters, or silicon halides, then growing the particles to colloidal size. The particles of colloidal silica thus obtained are generally spherical. Most of the inside particles form siloxane bonds (–Si–O–Si–), but the particle surface is covered with silanol groups (–SiOH).

[0012] In the present invention, one type of inorganic solid particles such as colloidal silica may be used mixed with a binder, or two or more varieties of inorganic solid particles may be used mixed with a binder. For the binder compounds to use in which the inorganic solid particles of the present invention are admixed, compounds with no compatibility problems can be used.

[0013] The solids content of inorganic solid particles such as colloidal silica in the binder is 0.001–20.0 weight%, preferably 0.01–5.0 weight%, and even more preferably 0.1–2.0 weight%. Amounts less than 0.001 weight% are not great enough to produce the resin impregnation enhancement effect of the inorganic solid particles, such as colloidal silica, since not enough of the particles become attached to the glass fiber. With amounts of more than 20 weight%, the binder cannot be applied to the glass fiber.

[0014] Yarn is manufactured from glass fiber strands on which a binder containing the inorganic solid particles of the present invention has been

applied, and since glass composition, filament diameter, cross-sectional shape of the filament, and number of filaments that make up a fiber bundle impose no limitations, any fiber bundles can be used. The solids content of the binder that contains the inorganic solid particles of the present invention and that is applied to the yarn is 0.001–10.00 weight%, preferably 0.1–4.00 weight%, and even more preferably 0.3–1.50 weight%. With less than 0.001 weight%, the binder is ineffective, whereas with more than 10.0 weight%, the fiber bundle hardens excessively, which causes problems in weaving the glass cloth.

[0015] The amount in the form of solids of inorganic solid particles attached to the glass fiber is 0.001–2.0 weight%, preferably 0.01–0.98 weight%, and even more preferably 0.1–0.6 weight%.

[0016]

[Actual Examples]

Actual Example 1

etherified high-amylose cornstarch	4.0 weight%
hydrogenated cottonseed oil	0.5 weight%
paraffin wax	1.0 weight%
polyoxyethylene polyoxypropylene ether	0.2 weight%
reaction product of tetraethylenepentamine with stearic acid	0.3 weight%
formalin (40 weight% solution)	0.1 weight%
colloidal silica (20 weight% solution)	0.5 weight%

[0017] 100 kg of binder of Actual Example 1 was prepared as follows: 4 kg of etherified high-amylose cornstarch was dispersed in 80 kg of water and the resulting dispersion was heated to 95°C, held for 30 minutes with stirring, and then cooled to 65°C (solution A). 500 g of heat-dissolved hydrogenated cottonseed oil, 1,000 g of paraffin wax, and 200 g of polyoxyethylene

polyoxypropylene ether were placed in a separate vessel, boiling water was added with stirring with a homomixer, and the resulting mixture was emulsified by reverse tumbling and then diluted with boiling water to obtain 5 kg of solution (solution B). Furthermore, 300 g of the acetic acid-activated product of a condensation product of tetraethylenepentamine with stearic acid was placed in a separate vessel and diluted with boiling water to obtain 3 kg of solution (solution C). Furthermore, 100 g of formalin was weighed out and then diluted with water to obtain 1 kg of solution (solution D). Moreover, 500 g of the colloidal silica "Snowtex ST-20" (produced by Nissan Chemical Industry Co., Ltd.; particle size 10—20 nm; SiO_2 20 weight%) was weighed out and diluted with water to obtain 5 kg of solution (solution E). Solution B, solution C, solution D, and solution E were added one after another to solution A, then enough water was added to adjust the total weight to 100 kg, and the resulting mixture was kept warm at 60°C.

[0018] This binder was then applied (0.90 weight% as solids) to glass fibers by a roller applicator and the treated glass fibers were bound into a glass fiber strand and wound off as a cake. Moreover, this strand was twined to obtain a yarn of G75 1/0 0.7Z. Next, this yarn was prepared for weaving with a high-speed warper (manufactured by the Sucker Co.), pasted with a pasting machine (manufactured by the Sucker Co.), and woven on a high-speed air jet loom (manufactured by the Tsudakoma Kogyo Co., Ltd.) to obtain glass cloth with weaving densities of 44 warps/2.5 mm and 32 wefts/25 mm. Furthermore, this glass cloth was heat deoiled to remove the paste, surface treated with silane coupling agent SZ6032 (produced by the Toray Dow-Corning Silicone Co., Ltd.) at a concentration of 0.3 weight%, then impregnated with FR-4 resin. Table 1 shows the stability of the shape of the cake and the quality of the

glass cloth; an extremely stable cake shape and excellent resin impregnation properties were demonstrated

[0019]

Actual Example 2

etherified high-amylose cornstarch	3.5 weight%
ordinary crosslinked cornstarch	1.5 weight%
hydrogenated cottonseed oil	1.0 weight%
paraffin wax	1.0 weight%
polyoxyethylene polyoxypropylene ether	0.2 weight%
reaction product of tetraethylenepentamine with stearic acid	0.4 weight%
formalin	0.1 weight%
colloidal silica (trade name: Cataloid S-30 H; produced by the Shokubai Kasei Kogyo Co., Ltd.; particle size 10–20 nm; SiO_2 content 30 weight%	0.5 weight% (as solids)

The processing procedure was the same as that of Actual Example 1, except that the above-mentioned binder was applied (0.97 weight% as solids) to glass fiber of G75. Table 1 shows the stability of the shape of the cake and the quality of the glass fiber cloth; an extremely stable cake shape and excellent resin impregnation properties were demonstrated.

[0020]

Actual Example 3

The processing procedure was the same as that of Actual Example 1, except that 0.4 weight% of soft calcium carbonate with an average particle size of 40 nm was used in place of the colloidal silica in Actual Example 1. The test results are shown in Table 1.

[0021]

Comparison Example 1

The processing procedure was the same as that of Actual Example 1, except that water was added in place of 0.5 weight% of colloidal silica. The results obtained are shown in Table 1.

[0023] [*misnumbered in the foreign -- Tr. Ed.*]

[Assessment Methods]

1. Cake Shape Stability

The appearance of the cake was observed by the naked eye, and the cakes were evaluated as those that were clearly deformed and those that were not.

2. Assessment of Fuzz

The fuzz on the surface of the product after twining and the fuzz on the surface of the glass fiber cloth woven by the loom was actually counted, then these two counts were graded 1 to 7, where 1 indicated the lowest fuzz count and 7 indicated the highest fuzz count. Grades of up to 2 or 3 were considered to be suitable for ordinary use.

[0024]

3. Resin Impregnation Properties

A constant amount (10 mL) of resin was dripped onto a glass fiber cloth (10 x 10 cm) which had been surface treated after heat deoiling, and the time until bubbles appeared in the glass fibers was recorded, then the results were graded 1 to 7; the lower the grade the better the results.

Composition of the Resin Used:

Epikote 1001 (epoxy resin produced by Shell Chemical Co.)	100 weight parts
dicyandiamide	2 " "
benzyldimethylamine	0.2 " "
methyl oxitol	100 " "

[0025]

[Advantages] According to the present invention, the distortion in external shape of a wound cake can be reduced; hence, there is less unwanted severing of the glass fiber obtained and there is less fuzz on the yarn and glass fiber cloth. Furthermore, solid particles are attached uniformly to the entire bundle of glass fibers that make up the glass fiber yarn; hence, when the cloth is woven, spaces between the fibers provided by the solid particles are secured in the yarn even in areas where the warp and weft are crossed at the highest densities, thus uniform resin impregnation and shortening of the impregnation time are made possible.

[0026]

TABLE 1. KEY: (a) Actual Example .... ; (b) Comparison Example 1; (c) shape stability (distortion); (d) no; (e) yes; (f) fuzz (score); and (g) resin impregnation properties (score).

		形状安定性 (c)(変形)	毛羽 (等級) (f)	樹脂含浸性 (等級) (g)
(a)	実施例1	なし(d)	1	1
(a)	実施例2	なし(d)	2	1
(a)	実施例3	なし(d)	2	2
(b)	比較例1	あり(e)	4	5

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(54)【発明の名称】　ガラス繊維用集束剤及びガラス繊維織物

(57)【要約】

【課題】樹脂含浸性の良いガラス繊維織物を提供する。

【解決手段】ガラス繊維を紡糸するとき付着させる集束剤中に５－２０００ｎｍのコロイダルシリカ、軽質炭酸カルシュウムなどの無機固体粒子を配合した。集束剤を付着させることによりヤーンを構成するガラス繊維の周囲に粒子が付着し隙間を作るので、このヤーンで製織した織物は樹脂の含浸性が良い。

【特許請求の範囲】
【請求項１】加熱脱油するガラス繊維用集束剤において無機固体粒子を含むことを特徴とするガラス繊維用集束剤。
【請求項２】ガラス繊維用集束剤中に平均粒子径が５－２０００ｎｍのコロイダルシリカ、軽質炭酸カルシュウム、カオリン、微粒タルクから選ばれた無機固体粒子を少なくとも１種類含むことを特徴とする請求項１記載のガラス繊維集束剤
【請求項３】請求項２記載の無機固体粒子が固形分で０．００１－２．０重量%付着しているガラス繊維ヤーンからなるガラス繊維織物。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は、ガラス繊維集束剤及びこの集束剤を付着させたガラス繊維に関するものである。
【０００２】
【従来の技術】ガラス繊維用集束剤は、溶融ガラスを高速で紡糸してガラス繊維にする際に、ガラス繊維を保護するため紡出直後の多数のガラスフィラメントにローラーアプリケーターやベルトアプリケーターにより塗布される。ガラス繊維用集束剤としては、ヤーン用とロービング用に大別される。以下ヤーン用集束剤について説明する。集束剤が塗布されたガラス繊維束は、円筒にケーキとして巻取られる。ケーキは適度に乾燥され、撚糸機により撚糸してボビンに巻取とりガラス繊維ヤーンとする。ヤーンは主に織物に製織され、集束剤を高温で加熱し酸化除去する熱脱油あるいは水洗、バイブロウオッシャーにより洗い流す水脱油などの脱油処理をした後、樹脂との接着性、耐熱性を向上させるシランカップリング剤などの表面処理剤をガラス繊維表面に付与するのが一般的である。
【０００３】このクロスに硬化していない樹脂を含浸させあるいは、溶剤を含み粘度を低下させた樹脂を含浸させ溶剤を除去後、積み重ねてプレスすることにより積層板に加工する。従来この目的に使用される集束剤は、繊維の毛羽立ちを防ぎ、しかも脱油しやすい澱粉を主体としたものが使われてきた。
【０００４】しかし最近はヤーン用集束剤の中にＰＶＡ（ポリビニルアルコール）、ウレタン樹脂、エポキシ樹脂など合成樹脂系の材料が使用される場合もある。使用される澱粉糊用の澱粉には種々の加工品があり、以下の態様のものを含んでいる。天然の未加工澱粉、例えばトウモロコシやジャガイモ（ポテト）等の澱粉、よびそれらの化学変性物、例えばヒドロキシアルキル化の様なエーテル化物、アセチル化の様なエステル化物、エピクロロヒドリン等の架橋剤によって反応せしめた架橋化物、酸処理など公知の澱粉分子量を小さくし、粘度を低くした低粘度化物等がある。これらの澱粉を使用した従来の集束剤の配合の一例を具体的に例示すれば、澱粉系材料、２重量%－１０重量%、潤滑剤、０．２重量%－５重量%、界面活性剤　０．０５重量%－１．０重量%、防腐剤　０．０１重量%－０．５重量%で残りが水で構成されている。
【０００５】澱粉は数百本のガラスフィラメントを１本のストランドに接着してまとめ、機械上のあらゆる屈曲及び摩擦から糸を保護するために皮膜形成の目的に使われている。澱粉の原料としてはトウモロコシ、ジャガイモ等がよく使われており、その化学変性物、例えばヒドロキシアルキル化の様なエーテル化物等がよく用いられている。潤滑剤はストランドに滑りを与え、機械上での摩擦を減少し糸を保護する目的で使われている。潤滑剤の種類としては、動植物油に水素添加した硬化油、パラフィンワックス、高級飽和脂肪酸と高級飽和アルコールのエステル等がよく用いられている。カチオン性潤滑剤は、ガラス糸を柔軟にしストランド中のフィラメント同士の摩擦等を減少させる目的に使われており、例えば、アルキル第４級アンモニウム塩や、ポリエチレンポリアミンと高級脂肪酸とを縮合反応させて得られるアマイドまたはイミダゾリン等がよく用いられている。界面活性剤は主に潤滑剤の乳化剤として使われており、例えば、ポリオキシエチレンアルキルエーテル等がよく用いられている。防腐剤は、ホルマリンが主に用いられている。
【０００６】固体粒子としてコロイダルシリカを配合したガラス繊維処理剤として、特公平１－２０３２４７号公報にはポリ酢酸ビニルにコロイダルシリカを配合したＦＲＰのスプレーアップ用のガラス繊維ロービングバインダーが開示されている。また特開平６－２４８５７２号公報にはコロイダルシリカをガラス繊維織物に含浸乾燥し、バイブロウオシャーによりガラス繊維織物を開繊し、その織物に樹脂を含浸、積層し加熱、加圧プレスする技術が開示されている。前者はコロイダルシリカを含む集束剤を付着させることによりガラス繊維ロービングを滑りにくくしカット性を向上させたものである。後者はガラス織物にコロイダルシリカを付与したのち、バイブロウオッシャーなどの手段で開繊処理する事によりガラス繊維の間にコロイダルシリカを入れ繊維間に隙間を設け樹脂の含浸を良くしようとするものである。しかしながら織物は経糸と緯糸がクロスしているので細かくみると均一にコロイダルシリカを入り込ませることはなかなか困難であった。
【０００７】
【発明が解決しようとする課題】このような化合物の組み合わせで構成された集束剤は、かなり優れた特性を持っており、実際今まで使われてきている。しかし、ガラス繊維の製造が高速化、高能率化され、次第に一度にガラス繊維を巻き取る量を増やし巻き取ったケーキを大きくする、ケーキのラージパッケージ化にともないケーキ内部の一部繊維の切断が起こりガラス繊維ヤーンの毛羽

立ちが増える、この現象は円筒の上に巻き取るガラス繊維が増えると直径が大きくなり、巻き取るとき次第にガラス繊維に掛る張力が増え内部のガラス繊維層を押し潰すような力が発生し一部のガラス繊維が切断されるものと思われる。あるいはガラス繊維を製織したガラス繊維織物に樹脂を含浸する時間を短縮し積層板の製造能率を上げ積層板の製造コストを低減したいという課題について解決が望まれている。

【０００８】本発明は、上記のような諸問題を解決するために新たに開発されたガラス繊維用集束剤に関するもので、ガラス繊維紡糸時に優れたケーキ形状安定性を有し、且つ、加工工程においても毛羽発生が巻取量を増加しても、従来の巻量の場合と同様に極めて少なく、製織されたガラス繊維織物の樹脂含浸性の良好なガラス繊維ヤーンを得ることのできる集束剤及びこの集束剤を付着させたガラス繊維を提供することを目的としている。

【０００９】

【課題を解決するための手段】本発明は、ガラス繊維用集束剤中にコロイダルシリカ、カオリン、軽質炭酸カルシウム、などの無機質固体粒子を少なくとも１種以上配合し、それらの固体粒子をガラス繊維に固形分で０．００１－２．０重量%付着させることにより上記の課題を解決した。

【００１０】

【発明の実施の態様】このような集束剤にコロイダルシリカなどの無機固体粒子を添加して前述の課題を解決しようとするものであるが、界面活性剤などにはコロイダルシリカと適合しないものがあり、これらを配合したときゲル化、分離などの起きる場合があり配合される集束剤の成分は、それを考慮して決められる。集束剤の成分が澱粉を主体とした従来のタイプのものに有効であるが、ＰＶＡ（ポリビニルアルコール）、ウレタン樹脂、エポキシ樹脂など合成樹脂系の材料が使用される場合も有効である。本発明に使用される無機固体粒子にはカオリン、軽質炭酸カルシュウム、微粒タルク、粉末状ヒュームドシリカ（日本アエロジル社製）、コロイダルシリカなどがある。これらの粒子は加熱脱油の温度で分解しないもので、粒子の大きさは５－２、０００ｎｍのものが使用できる。

【００１１】コロイダルシリカは粒子の大きさが５－１００ｎｍ程度である無定形シリカが水や有機溶媒に沈降せず安定に分散しているものであり、別名シリカゾルとも呼ばれている。このコロイダルシリカは、ケイ酸ソーダ水溶液（水ガラス）やケイ酸エステル、ハロゲン化ケイ素の加水分解等によって得られるケイ酸を、高重合化し、コロイドの大きさに成長させることによって得られる。このようにして得られるコロイダルシリカの粒子は、一般に球状であり、内部の大部分はシロキサン結合（－Ｓｉ－Ｏ－Ｓｉ－）であるが、粒子表面層はシラノール基（－ＳｉＯＨ）で覆われている。

【００１２】本発明はコロイダルシリカなどの無機質固体粒子一種を集束剤と混合して使用してもよく、二種以上の無機質固体粒子を集束剤と混合して使用してもよい。本発明の無機質固体粒子と混合して使用する集束剤用化合物には、相溶性に問題がないものであれば使用できる。

【００１３】集束剤中のコロイダルシリカなどの無機固体粒子の固形分含有量は、０．００１－２０．０重量%で、好ましくは０．０１－５．０重量%で、さらに好ましい量は０．１－２．０重量%である。０．００１重量%以下ではコロイダルシリカなどの無機固体粒子の樹脂含浸促進効果が出るだけの量をガラス繊維に付着させることが出来ず、２０．０重量%以上ではガラス繊維に塗布することが出来ない。

【００１４】本発明の無機固体粒子を含有する集束剤を付着させたガラス繊維ストランドからヤーンを製造するが、ガラス組成、フィラメントの直径、フィラメントの断面形、繊維束を構成するフィラメント数により限定されず、任意の繊維束に適用可能である。ヤーンに付着した本発明の無機固体粒子を含有する集束剤の固形分量は、０．００１－１０．００重量%で、好ましくは０．１－４．００重量%で、さらに好ましくは０．３－１．５０重量%である。０．００１重量%では集束剤としての効果がなく、１０．０重量%以上では繊維束が硬くなり過ぎガラスクロスを織る上で問題となる。

【００１５】ガラス繊維に付着している無機固体粒子は固形分量で０．００１－２．０重量%、好ましくは０．０１－０．９８重量%、更に好ましくは０．１－０．６重量%である。

【００１６】

【実施例】

＜実施例１＞

ハイアミロース型トウモロコシエーテル化澱粉	４．０重量%
水素添加綿実油	０．５重量%
パラフィンワックス	１．０重量%
ポリオキシエチレンポリオキシプロピレンエーテル	０．２重量%
テトラエチレンペンタミンとステアリン酸の反応生成物	０．３重量%
ホルマリン（４０重量%水溶液）	０．１重量%
コロイダルシリカ（２０重量%水溶液）	０．５重量%

【００１７】実施例１の集束剤１００ｋｇの調合方法は次の通りである。ハイアミロース型トウモロコシエーテル化澱粉４ｋｇを水８０ｋｇ中に分散させ、９５℃まで加熱し３０分間撹拌保持した後、６５℃まで冷却する

（A液）。別容器に、加熱溶解された水素添加綿実油５００ｇ、パラフィンワックス１０００ｇ、及びポリオキシエチレンポリオキシプロピレンエーテル２００ｇを秤量し、ホモミキサーで撹拌しながら熱湯を加え、反転乳化後、熱湯で希釈して５ｋｇとする（B液）。また、別容器に、テトラエチレンペンタミンとステアリン酸の縮合物の酢酸活性化物を３００ｇ秤量し、熱湯で希釈し３ｋｇとする（C液）。また、ホルマリンを１００ｇ秤量し、水で希釈して１ｋｇとする（D液）。さらに、コロイダルシリカ「スノーテックス：ＳＴ－２０」（日産化学工業（株）製、粒子径１０－２０ｎｍ、ＳｉO2 ２０重量%）５００ｇを秤量し、水で希釈して５ｋｇとする（E液）。A液にB液、C液、D液、及びE液を順次加えた後、水を加えて総重量を１００ｋｇに合わせ、６０℃で保温する。

【００１８】本集束剤をガラス繊維にローラーアプリケーターにより固形分で０．９０重量%付着させ、集束し、ガラス繊維ストランドにし、ケーキとして巻き取る。さらにこのストランドを撚糸し、Ｇ７５　１／００．７Ｚのヤーンとする。次いで、このヤーンを高速ワーパー（ＳＵＣＫＥＲ社製）で整経し、糊付機（ＳＵＣＫＥＲ社製）で糊付けし、高速エアージェット織機（津田駒工業（株）製）で製織し、織密度、経糸４４本／２５mm、緯糸３２本／２５mmのガラスクロスを作成する。さらに、このガラスクロスの熱脱油を行い、糊剤を除去した後、シランカップリング剤ＳＺ６０３２（東レ・ダウコーニング・シリコーン（株）製）を０．３重量%の濃度で表面処理を行い、ＦＲ－４樹脂に含浸させた。表１に、ケーキ形状安定性、ガラスクロスの品質を示すが、極めて安定したケーキ形状、そして、優れた樹脂含浸性を示した。

【００１９】＜実施例２＞

ハイアミロース型トウモロコシエーテル化澱粉	３．５重量%
通常型トウモロコシ架橋化澱粉	１．５重量%
水素添加綿実油	１．０重量%
パラフィンワックス	１．０重量%
ポリオキシエチレンポリオキシプロピレンエーテル	０．２重量%
テトラエチレンペンタミンとステアリン酸の反応生成物	０．４重量%
ホルマリン	０．１重量%
コロイダルシリカ（商品名：Ｃａｔａｌｏｉｄ　Ｓ－３０Ｈ、触媒化成工業（株）製、粒子径１０－２０ｎｍ、ＳｉO2 含有量３０重量%）　固形分換算	０．５重量%

本集束剤をＧ７５のガラス繊維に固形分で０．９７重量%付着させた他は実施例１と同様に実施した。表１に、ケーキ形状安定性、ガラス繊維織物の品質を示すが、極めて安定したケーキ形状、そして、優れた樹脂含浸性を示した。

【００２０】＜実施例３＞実施例１においてコロイダルシリカに代えて平均粒径４０ｎｍの軽質炭酸カルシュウムを０．４重量%使用したことを除いては実施例１と同様に実施した。試験結果は表１に示す。

【００２１】＜比較例１＞コロイダルシリカ０．５重量%の代わりに水を添加することを除いては、実施例１と同様に実施し、得られた結果を表１に示す。

【００２３】

【評価方法】

１、ケーキの形状安定性

ケーキの外観を肉眼により観察し明らかに変形しているものとそうでないものに区別した。

２、毛羽の評価

撚糸後の製品表面毛羽の本数、及び織機で織った後のガラス繊維織物表面の毛羽本数を数えて総合判定し、７ランクに分けたものであり、１が最も少なく７が最も多いこと示し、２－３以下であれば通常の使用には充分耐え得るものである。

【００２４】３、樹脂含浸性評価

熱脱油後表面処理されたガラス繊維織物（１０×１０ｃｍ）の上に一定量（１０ｍｌ）の樹脂を垂らし、ガラス繊維中の気泡が抜けるまでの時間を測定し、７ランクに分けたもので、値の小さい方が優れた結果の得られたことを示す。

使用樹脂組成

エピコート１００１（シェル化学社製エポキシ樹脂）	１００重量部
ジシアンジアミド	２　〃
ベンジルジメチルアミン	０．２　〃
メチルオキシトール	１００　〃

【００２５】

【効果】本発明によれば、巻き取ったケーキの外形の変形を少なくすることができるので、得られたガラス繊維の切断が少なくなり、ヤーン及びガラス繊維織物の毛羽が少なくなっている。またガラス繊維ヤーンを構成するガラス繊維の束全体に均一に固体粒子が付着しているので、織物にした場合経糸と緯糸が最も密度高くクロスする部分の糸にも固体粒子による繊維間の隙間が確保され

均一な樹脂含浸と含浸時間の短縮が可能となった。　　【００２６】

表１

	形状安定性 （変形）	毛羽 （等級）	樹脂含浸性 （等級）
実施例１	なし	1	1
実施例２	なし	2	1
実施例３	なし	2	2
比較例１	あり	4	5